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MONITORING AGENCY DOCUMENT NO.

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"Research on Electronically Excited States  
and Their Reactions"

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ANNUAL SUMMARY  
~~TECHNICAL (FINAL)~~ REPORT

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### Abstract

Several bridged-ring ketones have been synthesised having double bonds or aromatic rings with their  $\pi$ -electrons near the C of the C=O group. They all show intramolecular charge-transfer spectra. Molecules containing very strained cyclobutane rings have been made by photochemical isomerisation.

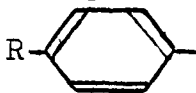
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During the year research has been concentrated on two overlapping fields: 1, synthesis of compounds that might show unusual electronic absorption spectra due to the proximity of electron donor and acceptor groups within the molecule - especially intramolecular charge-transfer spectra; and 2, photochemical preparation of strained molecules.

1(a) Attempts to make a series of derivatives of the diketone I (Cookson and Lewin, Chem. and Ind., 1956, 984) bearing substituents on the benzene rings, so that their ionisation potential could be systematically varied, were unsuccessful. An approach to related structures by photochemical 1:4-addition of cyclic dienes to the 9:10-positions of anthracene also failed. The ketone II, made by a rather tedious route involving addition of benzyne to cyclopentadiene as the first step, showed a well marked charge-transfer band as well as an unusually intense carbonyl band at 310  $\mu$ , but again the molecule did not readily lend itself to systematic variation. A somewhat restricted series of ketones III did show the expected trend

on variation of the electronic character of the benzene ring: the intensity of the band at about 310 mμ increased in the order  $R = \text{OAc} < \text{OH} < \text{OMe} < \text{O}^-$ , with extremes of  $\epsilon = 310$  to 3000.

Compared with a normal tetra-alkyl quinone or with its tetrahydro derivative, the spectrum of the quinone IV is shifted to longer wavelengths by about 30 mμ.

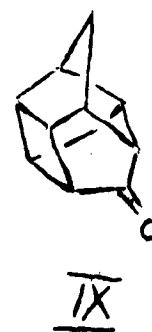
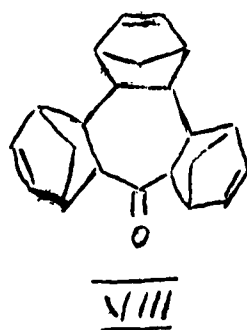
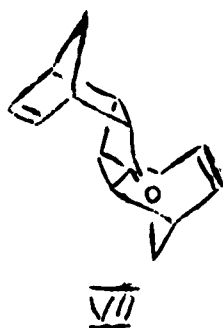
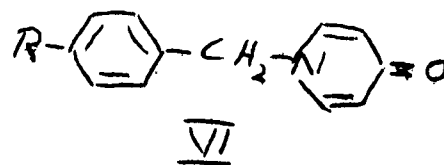
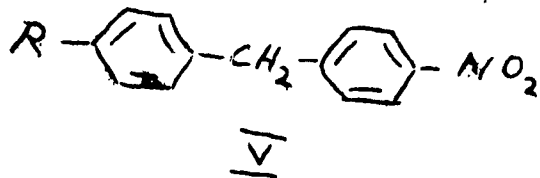
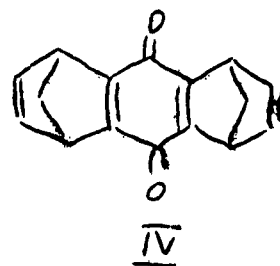
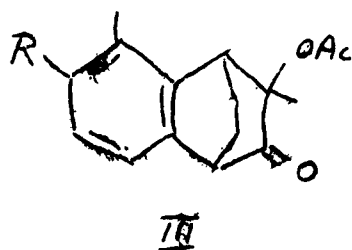
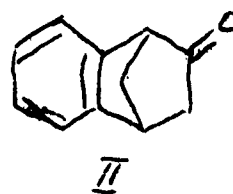
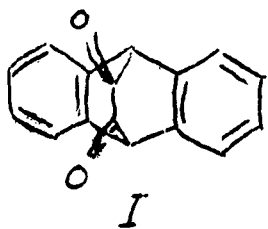
Since three-dimensional molecules containing variable donor and acceptor groups in the ideal geometrical arrangement for charge-transfer are difficult to synthesise, we have recently sought simpler systems that would allow wide variation in the donor and acceptor. Variation in the p-position of a benzyl group is unlikely to affect the conformation of a molecule, so that changes in absorption spectra not due to the chromophore  itself can be ascribed to electronic effects free from geometrical complications. The nitro-compounds V and pyridones VI show significant spectral changes with variation in R, but they are not large enough to be suitable for detailed analysis. We are exploring other possibilities of this sort.

1(b) In all the examples of intramolecular charge-transfer found so far the donor and acceptor groups are separated by only one saturated carbon atom. That allows ambiguities in interpretation. By developing a new way of making suitable bridged-ring ketones we have now provided examples of charge-transfer spectra where the donor and acceptor groups are further separated. Reaction of bicycloheptadiene with iron pentacarbonyl gives a ketone ( $\lambda_{\text{max}}$  222 mμ,  $\epsilon$  3,000) with the structure and stereochemistry shown in VII: evidently the anomalous u.v. band, which is absent in derivatives lacking either a double bond or a carbonyl group, arises from the excitation of a

$\pi$ -electron from C=C to an antibonding  $\pi$  orbital of the C=O. The ketone VIII, which cannot adopt the necessary orientation of double bond and carbonyl, whatever the conformation of the cycloheptanone ring, shows no such u.v. absorption. The ketone with two benzene rings or a quinone group in place of the two double bonds has also been obtained.

2. A variety of strained cage-molecules (Cookson, Crundwell and Hudec, Chem. and Ind., 1959, 1003) has been made by ultra-violet irradiation of bridged-ring dienes: the most strained is IX, containing a carbon atom common to two four-membered and one five-membered ring.

On irradiation, tetraphenylbutatriene dimerises to tetra-(diphenylmethylene)-cyclobutane, which, although not strictly a derivative of cyclobutadiene, does have four  $sp^2$  carbon atoms in a ring. Irradiation of the Diels-Alder adduct of cyclo-octatetraene and dimethyl acetylenedicarboxylate yields dimethyl phthalate and what is presumably a polymer of cyclobutadiene.



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Technical (Final) Report

RESEARCH ON ELECTRONICALLY EXCITED  
STATES AND THEIR REACTIONS

R.C. Cookson

27th January, 1960.

4 pages.

The University, Southampton, England.

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